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ScienceDirect
Scripta Materialia 65 (2011) 703–706
Scripta MATERIALIA
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Magnetic and structural properties of Ni–Mn–Ga Heusler-type microwires

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Received 27 May 2011; revised 3 July 2011; accepted 7 July 2011
Available online 14 July 2011

We report on the fabrication, and the magnetic and structural properties of novel glass-coated $Ni_{50.95}Mn_{25.45}Ga_{23.6}$ microwires with a metallic core diameter of 44 μm and a total diameter of 82 μm prepared by the Taylor–Ulitovsky method. These annealed microwires showed ferromagnetic behaviour with a well-defined easy axis that corresponds to the axis of the wire. X-ray diffraction confirmed a tetragonal martensitic structure with a lattice parameters a = 3.75 Å and c = 6.78 Å. The Curie temperature was estimated to be ~315 K. The maximum entropy change at the magnetic transition was $-0.7\ J\ kg^{-1}\ K^{-1}$.

Keywords: Glass-coated microwires; Magnetization curves; Magnetocaloric effect; Heusler alloys

Magnetic shape-memory alloys (MSMAs) have attracted particular interest in recent years owing to the significant magnetic-field-induced strain (MFIS), also referred as the "magnetic shape-memory effect" that originates from the coupling between magnetic and structural ordering. This strain arises through the magnetic-field-induced motion of twin boundaries [1–3]. Since the magnetic shape-memory effect is useful for actuation purposes, the inverse effect may be utilized for sensing and energy-harvesting applications [4]. The direct and inverse magnetic shape-memory effects cause magnetic field-induced superelasticity, which is the magnetically induced recovery of a large, mechanically induced deformation [5]. It is worth mentioning that the MFIS effect was described in the early 1990s in ferroelectrics (rare-earth molybdates) [6,7].

MSMAs usually exhibit a thermoelastic martensite transformation and may continuously change their shape between two states upon heating and cooling [7]. Consequently the martensitic transformation of MSMAs may be induced by stress. The coupling between magnetic and structural ordering in conjunction with the magnetic and structural transformations gives rise to further functional (i.e. non-mechanical) properties: the magnetocaloric effect, [8,9] the magnetic-field-induced martensitic transformation and its reverse transformation [10], giant magnetoresistance [11] and electric polarization [6,12].

Consequently, large MFIS values (up to 10%) have been reported for Ni–Mn–Ga single crystals, depending on their structure (grain size, size distribution) [13–15]. Usually small-grained polycrystalline Ni–Mn–Ga exhibits quite small MFIS (<0.01%), because grain boundaries effectively suppress twin-boundary motion [5]. Larger MFIS (2–9%) were also demonstrated in polycrystalline samples with high level of porosity [16].

From the point of view of technological applications, miniaturization of MSMA-based devices using small MSMA particles, wires, ribbons, films, bilayers and multilayers, and pillars is quite important [5]. On the other hand, in recent years particular attention has been paid to studying thin, glass-coated microwires produced by the Taylor–Ulitovsky technique. This method can produce glass-coated metallic microwires several kilometers in length with typical metallic core diameters ranging from 1 and 30 μm and with insulating glass coating thicknesses of between 0.5 and 20 μm. This method

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doi:10.1016/j.scriptamat.2011.07.018

allows a high quenching rate to be achieved and therefore can produce microwires with amorphous, nanocrystalline, microcrystalline or granular structures [17–20]. Amorphous and nanocrystalline microwires are especially suitable for a large number technological applications owing to their peculiar magnetic properties such as magnetic bistability and giant magnetoimpedance (GMI) [17–19]. Amorphous Co-rich microwires exhibiting the GMI effect have already been successfully used for low magnetic field detection by exploiting the high magnetic field sensitivity of the GMI effect [17–19].

Recently, this technique has been used to prepare microwires with a granular structure from (Co,Fe,Ni)–Cu alloys [18], as well as microwires that exhibit a mixed amorphous–crystalline structure [21], a magnetocaloric effect [17,22], a shape memory effect [23], and to produce microwires from Heusler alloys [17,21,24]. However, so far attention has mainly been paid to studies of amorphous, magnetically soft microwires [17–19].

In the case of Heusler-type microwires, their main advantage derives from the composite character of microwires, allowing production of relatively long pieces of microwire coated by glass, which is the case for brittle Ni–Mn–Ga alloy [5].

Consequently, the aim of this paper is to present results on using the Taylor–Ulitovsky method to fabricate Heusler-type $Ni_{50.95}Mn_{25.45}Ga_{23.6}$ glass-coated microwires a few meters long, with a metallic core diameter of 44 μm; initial studies of the structural and magnetic properties of these microwires are also presented.

The Heusler-type $Ni_{50.95}Mn_{25.45}Ga_{23.6}$ ingot used had been previously arc-melted from pure elements. Thin magnetic $Ni_{50.95}Mn_{25.45}Ga_{23.6}$ glass-coated microwires were fabricated by the Taylor–Ulitovsky method. The latest version of the Taylor–Ulitovsky process, described elsewhere [17–20], is based on direct casting from the melt. The composite microwires obtained were a few meters long and consisted of a metallic core with diameter, $d \approx 44$ μm, surrounded by a glass coating 18 μm thickness. After preparation, the Ni_2MnGa microwire was subsequently thermally annealed at 823 K for 5 min in a protective helium atmosphere.

Magnetic properties were studied using a SQUID Quantum Design MPMS XL within the temperature range from 10 to 400 K. Before recording the virgin magnetic curve, the sample was cooled down to 250 K at zero field and then heated up to the measuring temperature to maintain the same thermomagnetic history. The resistance was measured by the four-point method.

High-energy X-ray powder diffraction measurements were performed at HASYLAB at DESY (Hamburg, Germany) at the BW5 experimental station located on the DORIS III positron storage ring operating at an electron energy of 4.45 GeV and a stored current in the range of 140–100 mA. The sample measured at room temperature in transmission mode was illuminated for 60 s by a well-collimated 1 mm^2 incident beam of photon energy 100,577 keV ($\lambda = 0.12327$ Å). The corresponding XRD patterns were recorded by a 2-D detector (mar345 image plate). The background intensity was subtracted directly from the 2-D XRD pattern and the result was integrated to 2θ-space using the program Fit2D [12].

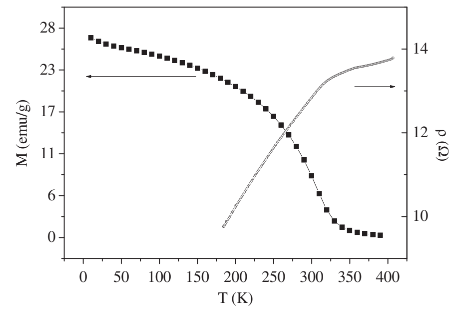

Figure 1. Temperature dependence of magnetization and resistance for $Ni_{50.95}Mn_{25.45}Ga_{23.6}$ microwires annealed at 823 K.

As-prepared microwires did not show ferromagnetic ordering. Annealing at 823 K (annealing time 5 min) resulted in a drastic change of magnetic properties: the annealed samples showed magnetization vs. temperature dependence typical for ferromagnetic behaviour with a Curie temperature of about 315 K (Fig. 1). The same Curie temperature can be estimated from the temperature dependence of the resistance. The resistance of a ferromagnetic conductor consists of a temperature-independent impurity contribution and two temperature-dependent contributions: a phonon contribution and a spin-disorder scattering contribution [25]. Above the Curie temperature the slope of the temperature dependence of resistance decreases significantly, due to the vanishing of spin-disorder scattering contribution (Fig. 1).

Such a drastic change of magnetic behaviour must be attributed to the strong internal stresses induced during the rapid solidification of the thin wire surrounded by the glass coating [17,18,26]. The internal stresses have mostly an axial component and are related to the difference in the thermal expansion of the metallic core and glass coating [26,27]. Therefore, the composite nature of these glass-coated microwires can introduce important changes in their structural and magnetic properties, taking into account that the martensitic transformation of MSMAs may be induced by stress, as mentioned in Ref. [5].

Analysis of the XRD allows us to identify that the crystalline structure is tetragonal martensitic structure with a lattice parameters $a = 3.75$ Å and $c = 6.78$ Å. However, the structure is elongated along the c axis (compared to bulk materials [28,29]). Unlike in previous studies of other Heusler-type CuGaMn microwires, we observed a single phase in the annealed microwires. We assume that the high levels of stress originating from the difference between the thermal expansion coefficients of the metallic core and the glass coating may be responsible for these deviations in lattice parameters.

The hysteresis loop measured in the longitudinal direction (i.e. parallel to the wire axis) shows an increase in magnetization up to a field of 3 kOe, above which the magnetization decreases (Fig. 2). The decrease in magnetization is a result of the diamagnetic contribution of the glass coating. The coercive field of ferromagnetic $Ni_{50.95}Mn_{25.45}Ga_{23.6}$ microwire is 100 Oe (see Fig. 2 inset).

However, the hysteresis loop measured perpendicular to the wire's axis (Fig. 3) shows a gradual increase in